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AND

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Strength Tests for Cement.

THE Institute for Technological Research of São Paulo, Brazil, has published, in Bulletin No. 11, the results of an investigation of methods of testing the strength of cement, and a specification is outlined. The investigators have studied the world-wide literature on the subject, and it has been their aim to establish a test which would classify cement from the standpoint of its concrete-making qualities. They have concluded that the compressive strength of a sand-cement mortar is approximately equal to that of a concrete providing that both be plastic and made with the same water-cement-ratio. The specification resulting from the investigation embodies the use of cylinders 10 cm. high by 5 cm. diameter for compression tests made with one part of cement to three parts of graded sand and sufficient water to give a standard consistency of mortar as judged by a flow table. The standard sand is a mixture in equal weights of four grades corresponding approximately to the British sieves 7/14 mesh, 14/25 mesh, 25/52 mesh and 52/100 mesh. Such a mixture obviously permits the use of a fairly high proportion of water in the mortar without segregation, and the specified consistency corresponds to about 12 per cent. of water on the mortar, or a water-cement-ratio of 0.48. Individual tests of cylinders differing by more than 10 per cent. from the mean of six results are discarded.

In a table comparing the results of numerous tests the correlation between standard mortar tests and concrete tests with the same water-cement-ratio is seen to be remarkably good, and the bulletin is worth the study of those interested in cement specifications. Compared with previously published results of attempts to design a mortar test that would give the same compression strength as concrete made with the same cement, the essential difference is in the grading of the sand and its greater fineness.

The Institute has also published in Portuguese a complete specification for Portland cement embodying the strength test described with minimum compressive strengths of 80, 150 and 250 kg. per square centimetre at ages of three, seven and twenty-eight days respectively. The other requirements of the specification call for no comment except that there are no limits to the lime content; 6 per cent. of magnesia is permitted and 4 per cent. loss on ignition.

The Late Henry Le Chatelier.

It is with much regret we record the death of Professor Henry Le Chatelier, who passed away on September 17 at the age of eighty-five.

Le Chatelier came of a family connected with the cement industry and well known for its scientific attainments. His own career was one of labour and sacrifice, and honours were deservedly awarded to him. In 1877, at the age of twenty-seven, he was elected Professor of Chemical Industry at the Paris School of Mines, having already spent six years at the *École Polytechnique* in research and served on a geological commission to Southern Algeria. In 1888 he was elected Professor at the *Collège de France*, and then followed a period of intense activity. He had already published a treatise on industrial heating, and he then found time to write a thesis on "Carbon, Silica, and Silicates." His work at this time, however, was even more noted for his brilliant inventions. The Saladin-Le Chatelier galvanometer is familiar to most chemists, while his thermo-electric and optical pyrometers are indispensable for the measurement of high temperatures.

But not only with his pyrometrical investigations has Le Chatelier aided the cement industry. His apparatus for ascertaining the soundness of cement and for determining its specific gravity are still in constant use throughout the world, while his theories on the essential chemical structure of Portland cement are notable for their originality and are still the subject of discussion amongst cement research workers.

In 1892, Le Chatelier was awarded the Jerome Ponty Prize, and in 1895 the La Caze Prize, while in 1911 he obtained the Bessemer Medal. The Iron and Steel Institute (England) elected him to its membership in 1904, and the Académie des Sciences followed suit in 1908. The services he rendered during the Great War by his researches on explosives and metals were very considerable, and he wore the ribbon of Commander of the Legion of Honour.

Possibly the triumph of his career came in 1922, when his fifty years of scientific work were recognised by the presentation of a gold plaque and 100,000 fr. The sum of money was at his express wish handed to the Académie des Sciences to found a scholarship.

In his later years Le Chatelier had to relinquish to a large extent his energetic career. When in his eightieth year he wrote to this journal: "At my age one begins to have the right to take a little rest. The young engineers and chemists of to-day should consider it their duty to undertake research work and make their results known the world over, as I in my time have done." The younger generation of cement engineers and chemists has in Le Chatelier an example of what one man can do to benefit an important industry; an inspiration to renewed effort to solve the problems still confronting the cement manufacturer and chemist.

Rapid Production of Pre-cast Concrete Units.

M. E. MOPIN'S NEW PROCESS.

REMARKABLE results have been achieved by Mons. E. Mopin, a well-known French concrete engineer, in the rapid production of pre-cast concrete units by a system of vibration which, with suitably graded aggregates, gives to the concrete a gelatinous nature which allows it to be turned out of the mould immediately without damage. One mould can therefore be used for a very large daily output, and consequently the cost of the mould is of little importance. As is shown in the accompanying illustrations, as soon as the mould is filled it is turned over on the floor and the mould lifted off without being dismantled, all cores and blocking-out pieces coming away with the base and sides of the mould.

During the last eight years a number of large housing schemes have been carried out in France on this system, of which the principal features are a light structural framework of steel units with pre-cast concrete floors, walls, partitions, staircases, balconies, ladders, linen cupboards, etc. At Bagneux and Vitry, suburbs of Paris, housing schemes on this system have been erected to the value of £400,000 and £200,000 respectively. At Drancy a housing scheme has lately been completed at a cost of £1,200,000, and at Leeds a slum-clearance scheme costing £400,000 is in progress. In all these the work was arranged on mass-production methods. The following notes describe the methods adopted by M. Mopin in the manufacture of pre-cast concrete units on these housing schemes.

Effects of Consistency of Concrete.

The methods of making plain or reinforced concrete products in common use are: (1) By compressing a dry or almost dry concrete, and (2) by using a fairly wet concrete which is tamped, or treated in some other suitable manner, to ensure that the steel is properly covered and that there are no spaces left unfilled.

In the first process the pressure applied to dry concrete enables the moulds to be stripped at once, and produces a compact concrete. As this concrete does not adhere well to the steel, the method is not suitable for reinforced products because the pressure subjects the reinforcement to movements which increase the voids in the concrete and cause a decrease in the bond between the concrete and the steel. Moreover, dry concrete adheres poorly to steel, and frequently the spaces between the bars are so small that thorough compacting is only obtained with great difficulty. Finally, compressed concrete requires a longer drying time and frequent watering, and the concrete is not at all elastic. If the concrete is made wetter it adheres well to the reinforcement, hardening occurs in better conditions than when dry concrete is used, and the resulting products are much more elastic. That the concrete may be wet enough to be poured without special precautions, however, an excess of water is required. This reduces the compactness and strength, and a richer mix is necessary. The moulds, also, can only be stripped from one to three days, according to the shape and size of the product. In consequence, this method involves the use of a large number of moulds to obtain a continuous output. In both these methods the removal of the moulds

takes place during or at the end of the setting time when the strength is still very low. In these circumstances if a crack forms during the removal of the moulds it will be permanent and may become wider after the product has matured and shrinkage has taken place with the result that products which appear sound when removed from the moulds develop cracks when they become hard. In a similar way products are often marred by slight chippings which cannot be easily repaired without damaging their appearance. Moreover, in both methods the moulds have to be dismantled, cleaned, and reassembled.

Manufacture by Immediate Removal of the Moulds.

To avoid the foregoing disadvantages experiments were made to find answers to the following problems: (1) The possibility of using a concrete which was sufficiently damp to give a plastic material, good adhesion to reinforcement, and favourable setting and hardening conditions. (2) To find a method of using this concrete which would ensure that the moulds would be properly filled, excess air and water removed, and a state, characterised by a combination of plastic consistency and cohesion, produced that would enable the concrete to have a stable form. (3) To secure immediate removal of the moulds so that the compactness of the concrete can be checked at once. If stripping is done before the set of the cement and while the concrete is plastic, there is no fear of cracks, since the products commence to set after the removal of the moulds and are not lifted again until they have hardened. On the other hand, any defect occurring when the mould is removed can be made good at once without difficulty because the concrete is still new, and these repairs leave little or no mark on the finished article. (4) A reduction in the number of men employed by working systematically. (5) A reduction of the cost of moulding products on large works. (6) The possibility of making very complicated products in a single expensive mould, because rapid production with one mould allows its cost to be written off very quickly. (7) Keeping the mould clean and reducing causes which tend to wear it out.

In the Mopin system a single mould, usually of wood, is used a very large number of times; its first cost is therefore unimportant, and no effort is made to avoid complicated moulds required to give the product the shape most suitable for its purpose and the least weight per unit. The moulds contain fittings to produce round edges, chamfers, etc., and are made so that reinforcement projects to connect adjacent products or to join them to the structural steel frame of buildings. As a rule there is no need to dismantle the outsides of the moulds; thus the cost of handling them is reduced. Holes in transmission-line poles are made by permanent cores. Part of the chamfers are obtained by movable pieces which are at once put back into the mould; the pegs which produce the holes for fixing the cross arms on poles are treated in a similar manner.

"Gelatinous" Concrete.

The object of the process is to make use of the gelatinous state obtained by vibrating concrete, which permits rapid and economical manufacture of products of all shapes and sizes by simply turning over the moulds on a suitable plain

surface and removing them before the cement begins to set. The process is as follows: A mixture of aggregate, sand, cement, and water gauged semi-wet is placed in a watertight mould. The mould is filled, the reinforcement being placed in position either before or while it is being vibrated. The concrete settles, driving the excess water and air to the top, and before setting commences the concrete attains a gelatinous plastic state. In this state it has the remarkable property of being able to be turned out of the mould by inverting the latter and lifting it away. The concrete retains the exact shape of the inside of the mould, and after the final set in ordinary conditions in free air undergoes no shrinkage or

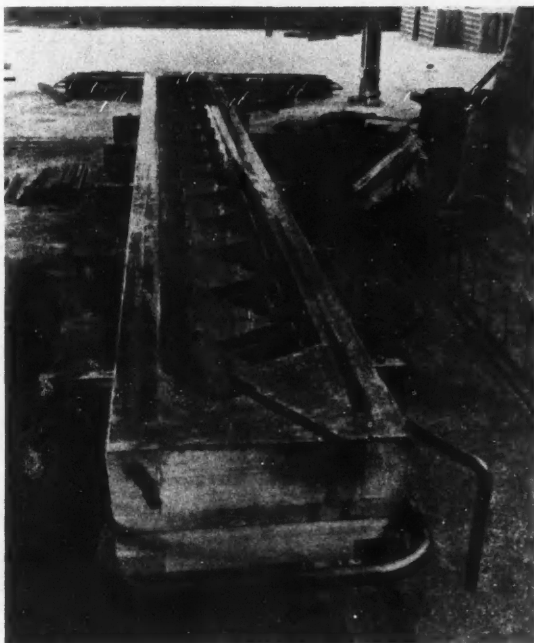


FIG. 1.—MOULD FOR STAIR STRINGER ON VIBRATING TABLE READY FOR FILLING. NOTE PEGS FOR FORMING HOLES IN THE CONCRETE. THIS MOULD IS TURNED OVER AND LIFTED FROM THE STRINGER WITHOUT BEING DISMANTLED.

sensible change of shape. While in the plastic gelatinous state it is deformable, like rubber or jelly, and no crack, chipping, or other defect occurs after the final set. If damage should occur owing to turning out the concrete roughly or due to defects in the moulds, it can be repaired without leaving any permanent marks on the products. The density and strength of concrete products made by this process are much higher than those made in other ways, and they may be reinforced if necessary.



FIG. 2.—MOULD AND SLAB LIFTED OFF VIBRATING TABLE.



FIG. 3.—MOULD AND SLAB LOWERED ON TO FLOOR.

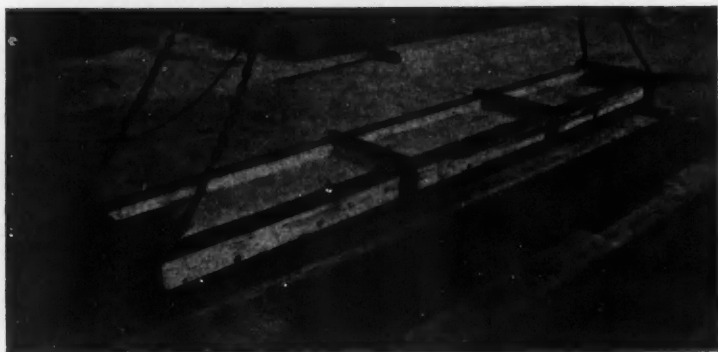


FIG. 4.—MOULD TURNED OVER AND LIFTED OFF FRESHLY-MADE SLAB
READY FOR RE-USE.

Concrete Materials.

The proportions of the aggregates used depend on their grading and their nature; whether they are siliceous, round gravel, or broken stone. As with ordinary concrete, preliminary tests are made to determine the minimum voids. The proportion of cement depends on its setting time and the use to be made of the product. For equal strength it is always less than is required with ordinary concrete. The quantity of gauging water used is just sufficient, allowing for the quantity in the aggregates, to obtain a concrete giving a slump of 0 to 8 mm. ($\frac{1}{8}$ in.), that is practically zero slump. The humidity of the concrete cannot be determined beforehand, since it depends on the quality and fineness of the cement, the size of the aggregates, and the proportion of inert materials incorporated in the mass to give the least voids. The quantity of water to be used is greater than is necessary to hydrate the cement, and is approximately the same as is required to obtain a plastic concrete. If too much water is used the excess is easily removed by prolonging the vibration. If there is not enough water none comes to the surface. In this case the plasticity of the concrete should be altered, for a concrete lacking plasticity does not become sufficiently fluid and lacks compactness. It is also difficult to remove the mould in such conditions.

Period of Vibration.

The arrival of the concrete at the gelatinous state required before turning it out of the mould is easily recognised by unskilled workmen. This is the case when the water comes to the surface of the concrete so that it has a viscous jellylike appearance and a pencil or a finger can be pushed into it to make marks which disappear as soon as the object making them is withdrawn. The length of time during which vibration is to be carried on depends on the size of the products being made, the nature and magnitude of the vibrations, and the mix and nature of the concrete. As an example and without laying down strict limits, the following are suitable figures when mechanically driven vibrating tables or electric vibrators are used with a concrete containing 770 lb. of ordinary Portland cement, 11.8 cb. ft. of sand between 5.55 mm. and 3 mm. ($\frac{1}{16}$ in. and $\frac{1}{8}$ in.), and 5.9 cb. ft. of gravel between 5 mm. and 15 mm. ($\frac{1}{8}$ in. and $\frac{5}{16}$ in.) when gauged with about 6 per cent. by weight of the materials of water.

The time of vibration necessary for a reinforced ribbed floor slab 36 in. by 20 in., containing 0.46 cb. ft. of concrete and weighing 70 lb., is from 25 to 30 seconds. The daily eight-hour output by one skilled man and two labourers with two double moulds and a vibrating table is 350 to 400 slabs in ordinary conditions. The time necessary for vibrating a reinforced tee-beam 13 ft. long containing 1.76 cb. ft. and weighing 275 lb. is from 1½ minutes to 2 minutes. The eight-hour production of one skilled man and three labourers with a vibrating table and two moulds is 90 to 100 beams. Reinforced concrete transmission-line poles 40 ft. long weighing a ton require to be vibrated for five to six minutes, and are made at the rate of 30 to 35 daily. Pierced fencing panels 6 ft. 6 in. by 4 ft. weighing 220 lb. are made at the rate of 40 to 50 daily by two men, and require

to be vibrated for three to four minutes each. These rates of production can be increased by installing plant to distribute the concrete in the moulds and by mechanical handling of the products.

Rate of Output.

The results obtained in France have come up to expectations, as may be seen from the following instances where the reinforcement was supplied ready for use and the concrete was delivered alongside the moulds.

(1) Pierced fencing panels about 6 ft. 6 in. by 4 ft. made by two men on one mould at the rate of 35 to 50 panels, or 230 lin. ft. to 400 lin. ft., daily. (2) Solid wall slabs with plain or ornamental faces made by two men at the rate of 120 sq. yd. daily. (3) Fence posts of different types made at the rate of 50 to 100 daily by one man using one mould. (4) Box sections for piers, weighing about 500 lb., made at the rate of 20 daily by two men with one mould. (5) Transmission-line poles, made at the rate of 40 poles daily with four or five men, or 18 to 25 poles daily with two or three men. The poles were 33 ft. to 40 ft. long and weighed from 1,300 lb. to 1,900 lb. (6) Signal posts for level crossings. Height 16 ft. 5 in. Designed for a load of 220 lb. at the top and a factor of safety of three. One man with one mould made 1,200 posts at the rate of 45 daily.

Advantages of the System.

The advantages claimed for this method are (1) continuous repetition in the use of the moulds and a high output, (2) reduction in weight and cost accompanied by high strength, and (3) reduction in the influence on the cost of the price of the moulds. Another advantage is that the quality of the products can be guaranteed, for they can only be turned out of the moulds undamaged if they have been properly made.

Any kind of cement can be used. At present M. Mopin uses Portland cement almost exclusively, but high-strength cements are used when necessary. Aluminous cements are only used if there is need of a very high strength or extra rapid hardening to facilitate handling the products and putting them in position.

No curing chamber is required. Instead the products are placed on a level concrete floor and exposed to the air directly after being removed from the moulds. In eight to twelve hours after being taken from the moulds they can be handled, turned over, and stacked. This time depends on the proportions of the concrete, the kind of cement used, and the air temperature. In winter the factory is heated so that the temperature of the area where the moulds are removed does not go below 36 deg. F.

The Mopin system of construction and the manufacture of vibrated concrete units in moulds that are stripped immediately are protected by patents in Great Britain.

Corrections to be Applied in Heat of Hydration Tests.*

By C. de LANGAVANT.

It has been shown that the ordinate at any point of the heat-loss curve represents, except for the factor $\frac{m}{a}$, the integral of the heating curve. This means that the ordinate of the heat-loss curve gives at each point a measure of the surface of the heating curve up to that time. If the observations are continued until the mortar has reached the ambient temperature the surface of the heating curve will be proportional to the total loss of heat and, as the difference of temperature is zero, this loss will be equal to the total amount of heat liberated. In a given apparatus the surface of the heating curve is proportional to the total heat liberated and can be used to measure it.

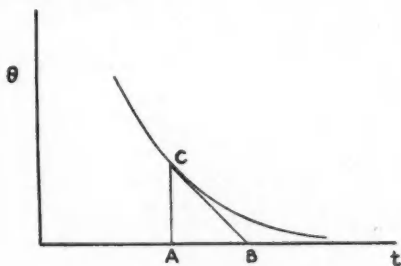


Fig. 4.

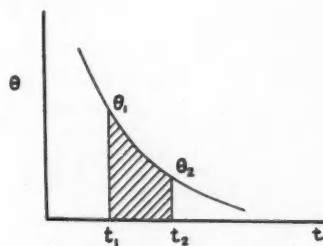


Fig. 5.

If water containing a certain amount of heat is placed in the apparatus and allowed to cool freely a cooling curve is obtained which follows the equation

$$\frac{d\theta}{dt} = -\frac{\alpha}{M} \cdot \theta$$

The function θ is the exponential function

$$\theta = e^{-\frac{\alpha}{M} \cdot t}$$

The subtangent (AB) at any point on the curve has a constant value $\frac{M}{\alpha}$ (Fig. 4),

and

$$\frac{d\theta}{dt} = \frac{AC}{AB} = -\frac{\theta}{AB}$$

And since

$$\frac{d\theta}{dt} = -\frac{\alpha}{M} \cdot \theta$$

it can be seen that $AB = -\frac{M}{\alpha}$.

This enables the exponential curve to be drawn if M and α are known.

* Concluded from October number.

The surface included between two ordinates of the curve is given by the integral

$$\int_{t_1}^{t_2} \theta dt = -\frac{M}{a} \cdot e^{-\frac{a}{M} \cdot t_2} + \frac{M}{a} \cdot e^{-\frac{a}{M} \cdot t_1} = \frac{M}{a} (\theta_1 - \theta_2).$$

If the heat loss curve is drawn for the flask filled with mortar it will be exponential and parallel to the cooling curve, and the loss of temperature will be $\theta_1 - \theta_2$ (Fig. 5).

The following rule can be used for finding the loss of temperature. The surface of the heating curve having been measured and expressed in degree-hours, it is sufficient to divide this surface by $\frac{M}{a}$ expressed in hours to obtain the loss of temperature suffered by the apparatus.

If the maximum temperature attained by a mortar with a water equivalent equal to m (including the container, thermometer, etc.) and the amount of cement present are known it is easy to calculate the heat liberated by a gram of cement. This method of determining the heat of hydration of cement is inferior to that of the adiabatic calorimeter because after four or five days the temperature of the mortar falls to practically atmospheric temperature. It is not certain that the reactions occurring at this relatively low temperature are as energetic as those at the higher temperature, but in any case it is only a question of velocity of reaction. If it is assumed that all the combinable elements react in the cement the quantity of heat liberated to arrive at complete combination is independent of the temperature. This result is obtained fairly rapidly if the reaction is completely adiabatic and all loss of heat is avoided. It will be obtained more slowly in a case where, however good the insulation, some loss of heat cannot be prevented. However, when the conditions of heat evolution in a large mass of concrete (such as a large dam) are examined it can be seen that they are different from those obtained in an adiabatic calorimeter. The concrete is not protected for some time after being placed and for the first few hours it can lose heat freely. It is only when the concrete has set, and has therefore lost more or less of its heat, that it is covered by fresh layers of concrete which prevent further cooling. After 24 to 48 hours it can be considered that the concrete is subjected to adiabatic conditions and the upper and lower layers heat up without exchanging heat with the intermediate layers. Hence if it is said that the thermos flask method does not reproduce the conditions of mass concrete the same may be said of the adiabatic calorimeter. The thermos flask method affords conditions sufficiently similar to those of mass concrete for most purposes.

After gauging the mortar at an ordinary or somewhat lower temperature, say 10 deg. C., the flask can be put in a vessel at 0 deg. C. in an ice chest or in melting ice. A heating curve is obtained which falls during the initial period. It is easy to trace the heat-loss curve, which will be the same as before using the same coefficient $\frac{M}{a}$ but the x-axis is placed at a temperature of 0 deg. C. After 24 or 48 hours (for example) the apparatus can be removed from the ice chest and the heating curve observed. It is interesting to compare this curve with the

curve obtained without freezing and it will be seen that the final temperatures are the same. As the reaction is affected by the initial freezing only in regard to velocity the two curves tend towards the same limit.

After having measured the loss coefficient of the flask, the latter is filled with a mortar of suitable consistency, say, 250 g. cement, 750 g. sand, and 145 g. water. Filling the flask with mortar is easy, but it is more difficult to introduce a neat paste on account of its viscosity. When the flask is nearly filled a small test tube is pushed into the mortar vertically for receiving the thermometer. A small amount of water or oil can be put into the test tube to distribute the temperature evenly. This precaution is particularly useful when a large number of tests is being made and the same thermometer is used for each. The thermometer should not be inserted into the mortar directly or it will stay fixed in it. During the liberation of heat water vapour condenses on the cork so that it becomes impregnated with water and hence becomes a good conductor. This is a source of error difficult to allow for, and it is better to avoid it by painting the cork with varnish, rubber solution, collodion, cellulose, or gold size. The cork itself is covered by an aluminium cap with a hole for the thermometer. Cracking of the flask has often been observed and is due to expansion of the cement; it stops the test because the temperature rapidly falls to that of the atmosphere, and is therefore immediately noticeable.

Following the suggestion of M. Marcotte, the heat of hydration can be used for rapidly identifying a binding material, particularly whether it is lime or cement. The heating curve is characteristic of the type of cement and will indicate the nature of the cement and its condition. For this purpose a very high degree of insulation is not necessary. Actually, with perfect insulation, adiabatic heating curves are obtained which are more or less alike and differ from one another only in the steepness of the ascending portion. With a comparatively poorly insulated apparatus, on the other hand, there is a maximum with a flat portion of extent depending upon the cement examined. For this type of test it is suggested that a thermos flask with a wide neck of $\frac{3}{4}$ -litre capacity should be used (as sold for picnic hampers). The cement is not put directly into the flask but in a removable receptacle. A cardboard cup of 400-g. capacity can be used for this; it is better, however, to use a slightly larger receptacle of cardboard or sheet iron which will hold 600 to 700 g. of mortar. The thermometer is protected by a test tube as before. It may be useful to use a maximum thermometer which will enable the maximum temperature attained to be observed easily. The insulation of this type of apparatus is not so good as that of a flask with a narrow neck. The loss from the neck is very large, and the utilisation of the internal space is less complete. The value of $\frac{m}{a}$ will therefore be smaller (of the order of five hours).

This reduction of the insulation makes the test less accurate because the cumulative loss is from four to five times greater than the rise in temperature, but this is a small matter as it is not the heats of reaction which are being measured but a comparison between cements which is being made. The use of a re-

movable receptacle has certain advantages. If the same apparatus is used each time the coefficient $\frac{m}{a}$ needs to be determined once only. With this it is easy to use a standard neat paste which it is almost impossible to introduce into a flask with a narrow neck. The liberation of heat is then more intense, which compensates somewhat for the lack of sensitivity of the apparatus. There is no fear of the flask breaking due to expansion of the cement or excessive rise in temperature. The cost of the test is very low and the preparation simple; in order to avoid the difficulties of continuous observation it is easy to make two tests of the sample of cement under observation with an interval of ten hours, and it is sufficient to record temperatures during the working hours. The curves thus obtained join up quite satisfactorily.

No attempt has been made to place any importance on the maximum point or the flat portion attained by the heating curve. This curve is solely the result of the liberation of heat and loss of heat. It is affected, among other things, by the inertia to heat of the mass. It seems to be impossible to trace the influence of all these factors. A cement which gives curve 1 (Fig. 6) for adiabatic conditions

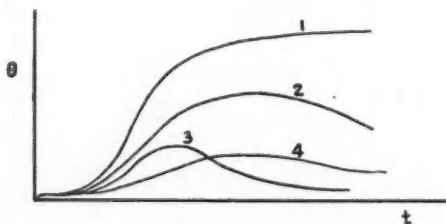


Fig. 6.

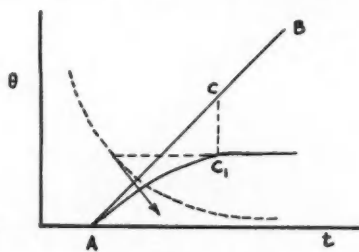


Fig. 7.

gives curves 2 or 3 according to the insulation of the apparatus and curve 4 if a mortar is used instead of a neat paste. It can be seen that the abscissa and ordinate of the maximum point can be very variable according to the conditions of the test.

A close examination of the heating curve discloses some interesting details. Let us assume that starting at A (Fig. 7) a reaction of constant intensity is produced in the apparatus. Then the liberation of heat (under adiabatic conditions) will be represented by a straight line. The heating curve will be represented by a curve tangent to AB at A and concave downwards. This curve will have a maximum at C_1 at the time when the temperature reaches the value for which the losses are equal to the liberation of heat. The tangent to the exponential curve for free cooling (for the same mass m) will have at this temperature θ the same slope as the straight line AB but the sign will be reversed. Starting with this instant, whatever the period during which the heat has been liberated the heating curve will be horizontal, i.e. there will be a flat portion. It can be seen

that if the ordinate of C_1 affords precise information about the slope of the straight line AB, i.e. the intensity of reaction, then the abscissa of the point C_1 has no significance. If at any instant B the liberation of heat ceases the curve of liberation of heat becomes a horizontal straight line BD (Fig. 8). There is a drop of temperature from the point B_1 which reproduces the curve of free cooling. The liberation of heat ABD will be represented by a curve $AC_1B_1D_1$. If, now, in the same apparatus a different intensity of reaction (e.g. greater) is produced the liberation of heat will be represented by a straight line MN whose slope will be greater than that of AB. The flat portion P_1N_1 (Fig. 9) of the heating curve corresponds to a temperature greater than that corresponding to the flat portion C_1B_1 (Fig. 8). After cessation of the liberation of heat at N there is a drop of temperature following the exponential curve N_1Q_1 . If it is assumed that the two reactions AB and MN liberate as a whole the same quantity of heat (during

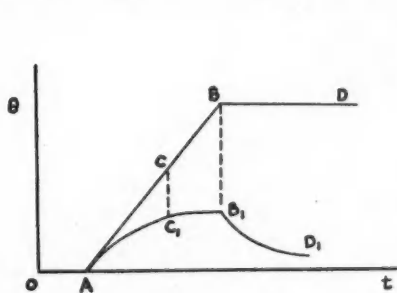


Fig. 8.

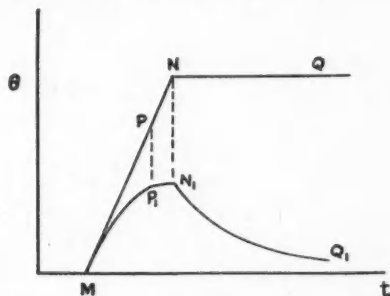


Fig. 9.

different times), this will be shown by the fact that the two points B and N will have the same ordinate. It has been shown already that for a given apparatus with the characteristic value $\frac{m}{\alpha}$ the surface of the heating curve represents the total cumulative losses, then at the instant when the cement reaches the ambient temperature this surface represents the total heat liberated and the surfaces of the two curves $AC_1B_1D_1$ and $MP_1N_1Q_1$ will be equal. In this case, instead of the heating curve having a flat portion of greater or less extent, there is a maximum and the curve is more or less angular at this point.

It has been assumed so far that the liberation of heat was sufficiently prolonged for the temperature of the mortar to attain the point of equilibrium where the addition of heat compensated the loss by radiation. It can happen, however, that the liberation of heat is intense and the duration short (the case of a cement with a rapid set). The quantity of heat liberated up to the end of the reaction will be too small and the mass to be heated too large, assuming a constant radiation loss, for the temperature to reach the point of equilibrium at which the flat portion is produced. At the instant the adiabatic curve reaches B the heating curve reaches B_1 only (Fig. 10), which is less than the temperature at the flat

portion. If at this instant the liberation of heat ceases the temperature falls exponentially and produces an angle at B_1 .

There is also the case in which two simultaneous reactions liberate heat, one which is intense and of short duration and the other less intense but more prolonged. The corresponding liberation of heat will be represented by the straight lines AB and AC (*Fig. 11*) assuming a common origin. The reasoning will be the same and the curve a little more complicated if the two reactions occur at different times. The total liberation of heat corresponding to the two reactions will be given by the line ADE. The heating curve will have a rising portion up to D_1 . It is assumed that the duration of the reaction is too short for the flat portion to be reached (quick setting cement). There is an angular portion at D_1 followed by a drop in temperature the rapidity of which, due to the liberation of heat, will be somewhat less than that corresponding to the curve of spontaneous cooling. The temperature will fall to the point F_1 , corresponding to an equilibrium between the addition of heat from the reaction AC and the loss of temperature θ . The temperature will then remain stationary up to the point

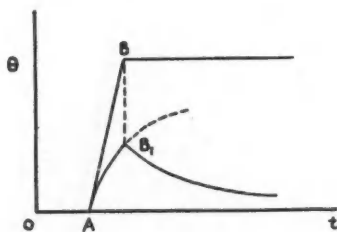


Fig. 10.

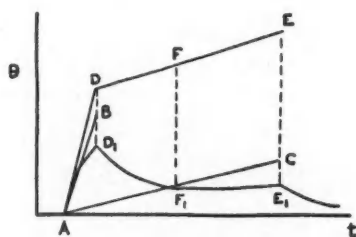


Fig. 11.

E_1 , where all liberation of heat ceases and the drop of temperature will follow the curve of free cooling.

It is evident that, in practice, the curves will not be so simple and clear as those which have been described. The reactions of hydration cannot be represented by straight lines. They do not start suddenly, acquire a constant intensity suddenly, and then end abruptly. The curves of liberation of heat obtained by correcting the heating curves have a double flexure, no angular point, and are asymptotic to the horizontal. The flat portions and minima represented in *Figs. 8 to 11* will in reality be less distinct.

In the study of quick-setting cements curves are sometimes obtained like those with an angular portion followed by a flat portion at a definitely lower temperature. This discontinuity in the curve is so marked that in the first test carried out by the author it was put down to an error of observation and corrected by making the curve pass through the other points. This effect is, however, explained by the differences in intensity of reaction at the two instants.

It is notable that the same cement which gives the curve in *Fig. 12* when the test is made on a neat paste in a wide-neck flask with $\frac{m}{\alpha}$ equal to five hours, gives a different curve (*Fig. 13*) for a 1 : 3 mortar in an apparatus which is well insulated and with $\frac{m}{\alpha}$ equal to 25 hours. The contradiction is apparent only. The quantity of heat liberated during the short reaction is insufficient to carry the mass of mortar to a temperature higher than the flat portion corresponding to the progressive reaction which prolongs the first, so that the maximum temperature of the mortar is observed only after several hours when the neat paste has already lost an important part of the temperature attained.

It can be seen also that, whatever be the type of apparatus used or the degree of insulation, there is slight delay in the heating curve. The curve can therefore be used to determine the time when the reaction commences.

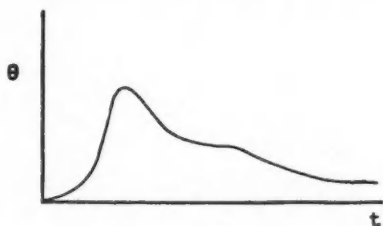


Fig. 12.

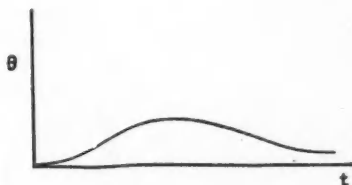


Fig. 13.

Useful information is afforded by the heating curves recorded in the same apparatus less well insulated but of known insulation constant $\frac{m}{\alpha}$; this may be set out as follows:—

(1) PERIOD OF COMMENCEMENT OF REACTION OA (*Fig. 14*).—This is given by the abscissa of point A starting with the ascending portion of the curve. As point A is not very well fixed by this it can be assumed that it is the point where the tangent at the point of inflexion of the curve meets the horizontal axis.

(2) INTENSITY OF REACTION B_1B_2 .—The ordinate of the maximum point measures the slope of the tangent to the curve of liberation of heat at point B . The position of point B on the curve of liberation of heat depends on the insulation of the apparatus. With poorly-insulated apparatus point B will nearly always be on the rising portion (apparently straight) of the heating curve, and the ordinate B_1B_2 will give the slope of this straight portion. From a study of the apparatus and the table of temperatures obtained the intensity of reaction can be calculated in calories/hour.

(3) DURATION OF THE REACTION AC_2 .—This is given by the total length of the ascending portion of the curve and the flat portion B_1C_1 . There will be an uncertainty about the choice of the point C_1 , because with well-insulated appa-

ratus the liberation of heat continues for more than eight days. It can be assumed that the point C_1 is given by the point whose ordinate is half that of point B.

(4) GENERAL SIGNIFICANCE OF THE LIBERATION OF HEAT.—It has been shown that the liberation of heat is represented by the surface of the heating curve and differs from it by the factor $\frac{m}{a}$. Having determined the constant $\frac{m}{a}$ for a given apparatus, it is sufficient to measure the surface of the heating curve either by a planimeter or other means, e.g. by weighing the curve drawn on card of known weight per unit area. The value of this surface expressed in degree-hours divided by $\frac{m}{a}$ in hours will give without further calculation the temperature which would be reached if all the heat liberated by the cement during hydration was used for heating the mass m (adiabatic conditions). The accuracy of the measurement depends only on the accuracy with which the constants m , a , and the surface has been determined. If an apparatus with a removable receptacle is used it is easy to obtain a comparison between uncorrected curves with different apparatus.

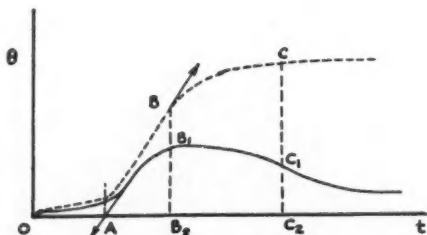


Fig. 14.

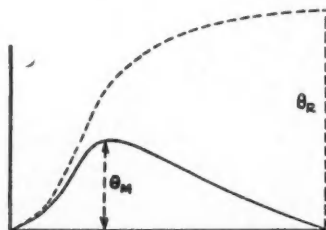


Fig. 15.

After accurately determining the constants a_1 , a_2 , etc., for the various flasks, and knowing the water equivalents m of the removable receptacles completely filled with neat paste (or mortar), it is easy to determine the water equivalents m_1 , m_2 , etc. (all less than m) thus:

$$\frac{m_1}{a_1} = \frac{m_2}{a_2} = \frac{m_3}{a_3} = \frac{m_4}{a_4}$$

m_1 , m_2 , etc., correspond to the weights p_1 , p_2 , etc., of the neat paste or mortar, which are easy to determine for each apparatus. It is not necessary to fill the receptacle completely. The weight p used for the test can be so calculated that all the flasks have the same value of $\frac{m}{a}$. It is evident that greater accuracy

will be obtained with better insulation of the apparatus, and the value of $\frac{m}{a}$ will be greater. Hence it is an advantage to make m as large as possible. The use of a cardboard cup shaped like a truncated cone, as used by the author in early experiments, is suitable only for studying the method. A removable iron

or cardboard receptacle should be used which is specially made for the purpose and which can have a capacity of 700 to 800 g. of paste for a flask of $\frac{1}{2}$ -litre nominal capacity.

If S is the total surface of the heating curve, $\theta_R = S \div \frac{m}{a}$ (Fig. 15) represents the temperature which the mass m will reach if all the heat liberated is used in heating it. The corresponding number of calories is $m\theta_R$. This liberation of heat is obtained by the hydration of q grams of cement. Then the heat of hydration is

$$\frac{m\theta_R}{q} = S \times \frac{m}{q} \div \frac{m}{a} = \frac{S}{q \times \frac{1}{a}}$$

It has been shown that there is a flat portion of the heating curve corresponding to a reaction of constant intensity liberating a quantity of heat equal to the heat radiated by the flask at the given temperature. This can be expressed in degrec-hours. The constant $\frac{m}{a}$ of an apparatus containing a mass m is the time required for the apparatus to lose a quantity of heat $m\theta$ for a constant difference of temperature θ . The flask therefore loses for unit temperature difference the quantity of heat $m\theta \div \frac{m}{a}$

It is known from the amounts used that m corresponds to a weight p of neat paste or mortar and to a weight of cement q . The existence of a flat portion on the heating curve corresponding to a difference of temperature θm , referred to the ambient temperature, shows that the reaction at this instant corresponds to the liberation of

$$\theta M \times \frac{m}{q} \div \frac{m}{a} = \frac{\theta M}{q \times \frac{1}{a}}$$

calories per gram of cement per hour. It should be noted that m is eliminated. Knowledge of the specific heat of the cement or mortar is of use only when the maximum temperature θ_R for adiabatic conditions is required.

A Method of Determining Clinker Quality.

IN a recent number of *Zement* (1936, p. 633), W. Anselm describes a method he has developed for determining the weight per litre of clinker from which the degree of burning and the quality of the clinker can be estimated. The method is as follows: about one litre of clinker retained between sieves with 5-mm. and 7-mm. holes (DIN) is taken immediately it leaves the cooler. This is allowed to flow in a uniform stream from the height of three or four inches into a vessel about 10 cm. high with a capacity of one litre. The surface of the clinker is levelled with a straightedge without exerting pressure on the mass. The weight of the contents of the vessel is the "litre-weight." The accuracy of the method is about ± 5 g.

The porosity of the clinker rises with falling "litre-weight." The "litre-weight" can be used for controlling the working of a kiln and has been tested at a works. It also shows irregularities in the working of a kiln. For a wet-process kiln it has been found that up to a "litre-weight" of 1.3 the clinker is underburned, from 1.3 to 1.5 it is well-burned, and over 1.5 it is strongly or over-burned. In general, the shape and chemical composition of the clinker have such a strong influence that for each type of raw material and kiln a set of figures must be collected from experience. If the iron oxide and alumina contents vary considerably, as is the case when blastfurnace slag is used, the method is not of much value but it is very useful for natural raw materials.

For good sound clinker the free lime content should be below 1.7 per cent. The strength drops when the "litre-weight" is greater than 1.5, hence the clinker must not be burned too hard. Hard burning also makes the clinker difficult to grind. For comparative grinding tests the "litre-weight" is a useful figure. It does not give much indication as to shrinkage, but hard burned clinker tends to give greater shrinkage. Further tests are required to elucidate this point.

Microscopical investigations show that with increasing "litre-weight" the tricalcium silicate increases in amount and size, the α -dicalcium silicate decreases in amount but the size remains the same, and the ground mass increases. Further research on this point, especially with artificial raw materials burned in laboratory kilns, should determine the dependence of the burning temperature on the "litre-weight."

A definite relation between the free lime content and the "litre-weight" was found. For values less than 1.25 the free lime increases very rapidly; for values of 1.25 and greater the free lime is 1.7 and less. There is also a close relation between the "litre-weight" and the expansion of the cement in the Le Chatelier soundness test, and it has been found that the limit lies at 1.25 when the expansion is 10 mm.

Rapid Method of Ascertaining the Silica Content of Portland Cement.

THE following note is from *The Chemical Trade Journal* :

If ammonium chloride is mixed with Portland cement before the cement is dissolved in hydrochloric acid, and the solution is then digested on a steam bath for thirty minutes, an accurate determination of silica can be made without the customary double evaporation of the solution. A method on these lines has been worked out by E. E. Maczkowske, of the U.S. National Bureau of Standards.

In this method (*J. Res. Nat. Bur. Stand.*, June, 1936), 0.5 gr. of cement and an approximately equal weight of ammonium chloride crystals are mixed thoroughly in a 50 cc. Pyrex beaker; the beaker is covered with a watch glass, and 5 cc. of hydrochloric acid (specific gravity 1.18) added carefully from a pipette, allowing the acid to run down the lip of the covered beaker. After the chemical action has subsided, the cover is lifted slightly and the mixture stirred with a glass rod, the cover is replaced, and the beaker set on a steam bath for thirty minutes. During this time of digestion the contents should be stirred occasionally and any remaining lumps broken to facilitate complete solution of the cement. A 9-cm. quantitative filter paper of medium fineness is fitted to a funnel, a small quantity of macerated filter paper (about the size of a large pea) is placed in the bottom of the cone, and the filter thus prepared is washed once or twice with hot water. The jelly-like mass of silicic acid is transferred as completely as possible, without dilution, to the filter, and the hydrochloric acid solution allowed to drain through.

Adhering particles in the beaker are loosened by means of a small rubber-tipped rod, and washed on to the filter with hot water; finally, the inside of the beaker is thoroughly wiped with a small piece of filter paper and this is placed in the filter. The mass is washed with small quantities of hot water, allowing each portion to run through completely, until the volume of the filtrate is about 125 cc. The determination is completed by the standard procedure.

To compare the results of this modified procedure with the conventional one, seven samples of cement of varying silica content were analysed by the two methods. The principal advantage of the modified procedure for the determination of silica in cement is that an analysis can be carried to the stage of igniting the silica in about an hour, instead of a day, thus expediting the determination of silica and also the preparation of the solution for the determination of other constituents. There may also be a gain in accuracy.

Although the present study of the effect of ammonium chloride on the determination of silica has been limited to the analysis of Portland cement, there appears to be no reason, states the author, why its use cannot be extended to other siliceous materials which are decomposed by acids in preparation for analysis.

Studies on Ore (or Iron) Cement.

By SHOICHIRO NAGAI, KENJI NOMI and KIYOSHI INOUE.

THE authors have reported further results of studies comparing high-iron-oxide special Portland cements [ore cement (Erzzement), iron cement (Eisenzement), Kalicrete cement, Ferrari or Brownmillerite cement, Kühl cement, etc.] with ordinary Portland cement and various mixed Portland cements. The expansion or contraction during the hardening of cement-sand mortar were tested by prismatic test pieces (4 cm. by 4 cm. by 16 cm.) of 1 : 1 : 2 plastic mortar, cured in water, in 10 per cent. Na_2SO_4 and in 10 per cent. NaCl solutions for 35 (3 + 32) weeks. The results are given in Table I.

TABLE I.—EXPANSION OR CONTRACTION OF MORTARS OF VARIOUS CEMENTS CURED IN WATER AND SALT SOLUTIONS.

Type of Cement	Curing solution	Expansion (+) or contraction (−) after preliminary hardening 2 weeks in water and 1 week in warm (50 deg. C.) water (mm/10m.)				
		4 weeks	12 weeks	20 weeks	26 weeks	32 weeks
Portland cement ..	Water	+10.7	+10.0	+2.1	+2.1	+5.0
	10% Na_2SO_4	+2.9	+12.9	+52	+77	+91
				(Considerably cracked)		
Mixed Portland cement	10% NaCl	+10.7	+11.0	+7.1	+12.1	+6.4
	Water	−2.9	−1.4	−2.9	−1.4	−2.9
	10% Na_2SO_4	+7.9	+6.4	+5.7	+11.4	+10.0
	10% NaCl	+2.9	+5.7	+7.9	+10.7	+9.3
" " "	Water	−2.1	+4.3	+4.3	−1.4	−2.1
	10% Na_2SO_4	+7.1	+8.6	+4.3	+7.1	+6.4
	10% NaCl	+1.4	−3.6	+0.7	−0.7	+2.1
	Water	+4.3	+8.6	+10.7	+8.6	+7.1
Iron cement ..	10% Na_2SO_4	−0.7	+1.4	+1.4	−2.1	0
	10% NaCl	−5.0	−1.4	−5.0	−3.6	−2.9
	Water	+4.3	+6.4	+3.6	+5.0	+5.7
	10% Na_2SO_4	+7.1	+6.2	+5.9	+7.0	+6.6
" " "	10% NaCl	+3.6	+2.9	+4.3	+2.9	+3.9
	Water	+5.7	+2.9	+6.4	+2.9	+2.9
	10% Na_2SO_4	+14.3	+20.0	+15.0	+12.9	+11.4
	10% NaCl	0	0	0	−4.3	−2.1
Kalicrete cement ..	Water	−1.4	+2.1	+7.9	+5.0	+5.0
	10% Na_2SO_4	+2.1	+5.7	+6.4	+3.6	+4.3
	10% NaCl	−1.4	+2.1	0	−1.4	+0.7
	Water	+1.4	+6.1	+5.7	+5.0	+4.3
" " "	10% Na_2SO_4	+5.7	+2.9	+7.1	+8.6	+7.5
	10% NaCl	+4.3	+5.0	+6.4	+7.5	+5.7
	Water	+11.5	+5.7	+4.3	+9.3	+7.0
	10% Na_2SO_4	+17.1	Disintegrated	"	"	"
Kühl cement ..	10% NaCl	+2.9	+2.1	+0.7	−1.4	+2.1

It is seen from these results that high-silica mixed Portland cement is very stable, and iron cement and Kalicrete cement are more resistant than common Portland cement and Kühl cement of high alumina content.

Corrosive action on mortar strengths of prismatic test pieces cured in water, 10 per cent. Na_2SO_4 , or NaCl solution for 35 (3 + 32) weeks were tested by comparing the bending and compressive strengths after measuring their expansion or contraction. The results were compared with those cured in water for four

or 35 weeks and are shown in Table 2. It is seen that mixed Portland cements considerably increased in strength even by curing in aggressive salt solutions, and iron cement and Kalicrete cement are more resistant to the aggressive solutions than common Portland cement.

TABLE 2.—STRENGTH TESTS OF MORTARS CURED IN WATER OR AGGRESSIVE SALT SOLUTIONS.

Type of cement	Curing solution	Strength (kg/cm ²) and Index			
		Bending strength kg/cm ²	Index	Compressive strength kg/cm ²	Index
Portland cement ..	Water	76.5 (57.9)	100	531 (320)	100
	10% Na ₂ SO ₄	7.2	9.4	107	20
	10% NaCl	85.8	112	503	95
Mixed Portland cement ..	Water	87.2 (58.5)	100	453 (325)	100
	10% Na ₂ SO ₄	99.3	114	452	100
	10% NaCl	113.7	131	456	100
" " " "	Water	87.0 (44.4)	100	447 (265)	100
	10% Na ₂ SO ₄	98.5	113	466	104
	10% NaCl	106.3	122	476	106
Iron cement ..	Water	68.4	100	349	100
	10% Na ₂ SO ₄	75.5	110	352	101
	10% NaCl	68.0	100	343	98
" " " "	Water	56.6	100	344	100
	10% Na ₂ SO ₄	71.6	126	372	108
	10% NaCl	62.5	110	348	101
" " " "	Water	53.1	100	318	100
	10% Na ₂ SO ₄	62.9	119	370	116
	10% NaCl	55.4	104	355	112
Kalicrete cement ..	Water	67.5	100	418	100
	10% Na ₂ SO ₄	75.1	111	485	116
	10% NaCl	66.6	98	408	98

(The numbers in brackets are the strengths after water curing for four weeks.)

Two samples of high-iron-oxide special Portland cements, of iron cement (No. 411) and of Kalicrete cement (No. 412) were prepared from various raw materials of limestone, clay or ganister, copper slag, or pyrite cinder. To these two samples were added two other cements, No. 389 of common Portland cement and No. 413 of high-silica mixed Portland cement, for comparative tests. The chemical compositions, specific gravities, setting times, etc., were determined and compared as shown in Table 3.

TABLE 3.—COMPARISON OF CHEMICAL COMPOSITIONS, SPECIFIC GRAVITY, FINENESS, AND SETTING TIME.

No.	Type of cement	Loss on ignition (%)	Insol. Res. %	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	SO ₃ (%)	Free lime (%)	Sp. Gr.	Finesness residue on 4900-mesh sieve	Setting time	
													Initial	Final
389	Portland cement	1.16	0.62	22.31	5.20	3.30	64.27	1.25	1.28	0.61	3.15	4.8	br. min. 2-23	hr. min. 4-20
413	Mixed Portland cement	3.08	24.95	41.29	7.98	2.52	42.45	1.22	1.19	0.49	2.72	4.8	2-45	4-55
411	Iron cement	0.90	0.18	21.76	2.58	8.37	64.05	0.84	1.47	1.44	3.22	5.7	1-34	2-42
412	Kalicrete cement	0.17	0.30	22.78	4.96	6.17	62.90	0.94	1.48	0.51	3.23	6.6	2-22	3-31

These cements were tested for strengths by (a) 1 : 3 cement-standard-sand mortar and (b) 1 : 2 cement-fine-sand plastic mortar, and then compared on their temperature rise during setting and hardening in a small Dewar's glass vessel. The mixed Portland cement (No. 413) evolved the least heat, followed by high-iron-oxide special Portland cements of the iron cement and Kalicrete cement type, which are more suitable for mass concrete works than common Portland cement.

The research is being carried out at the Institute of Silicate Research, Imperial Tokyo University, Japan.

[Previous reports on this subject were published in "Cement and Cement Manufacture" for June and September 1935, and April 1936.]

The System $\text{CaO-Fe}_2\text{O}_3$.

An account of a research on the system $\text{CaO-Fe}_2\text{O}_3$ has been published by B. Tavasci. The brochure comprises ten pages, and deals with compounds of lime and iron oxide produced at high temperature, in relation to the equilibrium diagram. The brochure is printed in the Italian language.

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